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Cobalt carbonyl catalyzed carbonylation of benzal bromides by phase transfer catalysis

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Abstract

The reaction of benzal bromides with Co (1 atm) in a binary system (aq. KOH/C_6H_6) in the presence of a catalytic amount of $Co_2(CO)_8$ together with benzyltriethylammonium chloride as a phase transfer catalyst for 8 h at room temperature gives the corresponding carboxylic acids in good to excellent yields.

Introduction

Despite the current widespread upsurge of interest in the selective carbonylation reaction catalyzed by cobalt carbonyl complex [1], much investigation has shown recently that the phase transfer catalysis is an exceedingly useful technique in organometallic chemistry [2]. One of the useful phase transfer reactions is the carbonylation of organic halides such as benzyl or allyl halides in the presence of cobalt carbonyl at room temperature under one atmospheric pressure of carbon monoxide, to give carboxylic acids. The acylcobalt carbonyl complex generated from $Co_2(CO)_8$ is assumed to be the key intermediate in these reactions. The above mentioned work has been carried out primarily by Alper [3–5], Foà [6–8], and by us [9,10]. Little attention has been paid to catalytic carbonylation of benzal bromides by dicobalt octacarbonyl under phase transfer catalysis. Here we report on a simple method for the carbonylation of aryl dihalides using benzal bromide as a typical example.

Results and discussion

Treatment of benzal bromides (I) with CO (1 atm) in the presence of catalytic amounts of both $Co_2(CO)_8$ and benzyltriethylammonium chloride using a binary

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Table 1

$Co_2(CO)_8$-phase transfer catalyzed carbonylation of benzal bromides.

Entry No.	Substrate ($XC_6H_4CHBr_2$) X =	PTC [a]	Product [b]	Yield (%) [c]
1	*p*-Cl		*p*-$ClC_6H_4CH_2COOH$	29
2		18C6	*p*-$ClC_6H_4CH_2COOH$	32
			(*p*-ClC_6H_4CH=$)_2$	39
3		18C6/TEBA	*p*-$ClC_6H_4CH_2COOH$	70
			(*p*-ClC_6H_4CH=$)_2$	12
4		TEBA	*p*-$ClC_6H_4CH_2COOH$	92
5 [d]		TEBA	*p*-$ClC_6H_4CH_2COOH$	91
6 [e]		TEBA	*p*-$ClC_6H_4CH_2COOH$	20
7		CTMA	*p*-$ClC_6H_4CH_2COOH$	20
8		TBAH	*p*-$ClC_6H_4CH_2COOH$	24
9 [f]	*o*-Cl	TEBA	*o*-$ClC_6H_4CH_2COOH$	34
10	*p*-CH_3	TEBA	*p*-$CH_3C_6H_4CH_2COOH$	94
11 [f]	*o*-CH_3	TEBA	*o*-$CH_3C_6H_4CH_2COOH$	67
12	H	TEBA	$C_6H_5CH_2COOH$	93

[a] 18C6 = 18-crown-6-ether; TEBA = benzyltriethylammonium chloride; CTMA = cetyltrimethylammonium chloride; TBAH = tetrabutylammonium hydrogen sulfate. [b] Products were identified by comparison of properties (e.g., IR, NMR (^1H, ^{13}C), mass spectrum) with those of authentic samples. [c] Yields are of isolated, pure products and are based on reactant bromide. [d] Molar ratio: substrate/$Co_2(CO)_8$/PTC = 20/3.0/1.0. [e] 60 °C. [f] 12 h.

system (aq. KOH/C_6H_6) for 8 h at room temperature gives the corresponding carboxylic acids (II) in good to excellent yields (e.g., X = *p*-Cl, 91% (entry 5); X = H, 93% (entry 12); X = *p*-CH_3, 94% (entry 10)), although in some cases the yields were lower (e.g., X = *o*-Cl, 34% (entry 9); X = *o*-CH_3, 67% (entry 11)). Consequently, for the

$$\underset{\text{(I)}}{XC_6H_4CHBr_2} + H_2O + CO \xrightarrow[\text{aq. } KOH/C_6H_6,\ 8\text{ h, r.t.}]{Co_2(CO)_8,\ PhCH_2(CH_3CH_2)3N^+Cl^-} \underset{\text{(II)}}{XC_6H_4CH_2COOH}$$

X = H; *p*-, *o*-CH_3; *p*-, *o*-Cl

substituted benzal bromides, substituents such as the methyl and chloro groups have almost no effect on the formation of the carboxylic acids when located at the *para* position, but they show some inhibition when located at the *ortho* position. *o*-Methyl and *o*-chlorobenzal bromides require longer reaction times for completion than the *para* derivatives. The influence by the *ortho* substituents is probably because of steric hindrance.

In Table 1 are listed the results obtained in the carbonylation of benzal bromides. Without the phase transfer catalyst, the product yield was low (entry 1). In the presence of 18-crown-6 ether as a phase transfer catalyst, 4-chlorophenylacetic acid and 4,4′-dichlorostilbene were formed almost equally from 4-chlorobenzal bromide by using 20/7.0/3.0 ratio of substrate/metal carbonyl/phase transfer catalyst (entry 2). A 1.0/1.0 ratio of benzyltriethylammonium chloride/18-crown-6-ether, 4-chlorobenzal bromide gives mainly the corresponding carboxylic acid, 4-chlorophenylacetic acid (entry 3). Surprisingly, by using only benzyltriethylammonium chloride, the product was obtained in 92% yield (entry 4); a decrease in the molar ratio of cobalt catalyst from 7.0 to 3.0, still gave the product in 91% yield (entry 5). The use of cetyltrimethylammonium chloride or tetrabutylammonium hydrogen sulfate in place of benzyltriethylammonium chloride as a phase transfer agent resulted in lower product yields (20 and 24%, see entries 7 and 8). At elevated temperatures the yield of product was reduced inversely (entry 6). All of these reactions gave the corresponding carboxylic acids as the major products or the sole products. Sometimes the intermediate products α-bromophenylacetic acids, were formed in 3–5% yields, but benzyl bromides or double carbonylation products were not. Mechanistic study for these reaction results is under way.

Experimental

The following typical procedure is as follows: benzyltriethylammonium chloride (0.07 g, 0.30 mmol) was dissolved in 20 ml of 5 *M* KOH and 20 ml of benzene under nitrogen, and the solution was stirred at room temperature for 30 min. 4-Chlorobenzal bromide (0.57 g, 2 mmol) in benzene solution (10 ml) was added to the above solution, and then $Co_2(CO)_8$ (0.10 g, 0.30 mmol) was carefully added. The gas above the mixture, nitrogen, was replaced with carbon monoxide, and the mixture was vigorously stirred for 8 h. The layers were separated, the aqueous phase was acidified with dilute hydrogen chloride, and extracted with diethyl ether (3 × 20 ml). The etherial extract was dried ($MgSO_4$), and concentrated. Preparative thin layer chromatography on silica gel gave a pure 4-chlorophenylacetic acid (0.31 g, 91%).

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References

1 M. Foà and F. Francalanci, J. Mol. Cat., 41 (1987) 89.
2 H. Alper, Adv. Organomet. Chem., 19 (1981) 183.
3 H. Alper and H. des Abbayes, J. Organomet. Chem., 134 (1977) C11.
4 S. Gambarotta and H. Alper, J. Organomet. Chem., 212 (1981) C23.
5 H. Alper, J. Organomet. Chem., 300 (1968) 1.
6 L. Cassar, M. Foà, and A. Gardano, J. Organomet. Chem., 121 (1976) C55.
7 L. Cassar and M. Foà, J. Organomet. Chem., 134 (1977) C15.
8 F. Francalanci, E. Bencini, A. Gardano, M. Vicenti, and M. Foà, J. Organomet. Chem., 301 (1968) C27.
9 S.C. Shim, W.H. Park, C.H. Doh, and H.K. Lee, Bull. Kor. Chem. Soc., 9 (1988) 61.
10 S.C. Shim, W.H. Park, C.H. Doh, and J.O. Baeg, Bull. Kor. Chem. Soc., 9 (1988) 186.